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Improvement on Wet Strength of Handsheets by Heat Treatments

By

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熱処理によるパルプ紙葉の湿潤強度の向上

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Introduction

The demand of paper and its products has annually increased in various fields. The conventional paper, however, is easy to get wet and loses strength

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and dimensional stabilization by soaking in water. During the period when the paper was used almost exclusively for writing and printing, the presence of wet strength was of little importance. It has lately been stated that paper products could be much more useful if they would be improved on such problems. For these purposes, papers treated mainly with synthetic resins to give them wet strength have gradually been applied in special packages, maps, paper towels, food wraps, building papers and so on.

On the wet strength agents, there have been many studies, such as addition of urea-formaldehyde^{16),18),25),31),32),34),40),46)} and melamine-formaldehyde resins^{6),21),29),39),43),45)}, dialdehyde starch^{2),5),10),11),14),15),22)~24),41),44)} or graft-copolymerization with synthetic polymers^{3),8),9),17),19),28)}.

The present investigation dealt with heat treatment of handsheets to improve the wet strength and dimensional stability, because the method seemed to be easier and more economical than the other methods. The process has already been employed widely for fiberboard industry. As for paper of this type there are also U.S. patents³⁰⁾. The nature of wet strength paper developed by heat treatment or catalyzed heat treatment has been studied by YOSHINO^{47),48)}, LOREY²⁰⁾, STAMM³³⁾, COHEN⁷⁾, OTA²⁶⁾, TAKE³⁵⁾, TEDER³⁸⁾, BATES¹⁾ and HECHLER¹³⁾. It has been reported that the heat treatment showed promise as a means of dimensionally stabilizing paper and of giving it wet strength, but that it should be limited to applications where some embrittlement is permissible³³⁾. With this limitation in view, authors studied to find out the effect of heat treatment on physical properties of pulp handsheets of different chemical composition, and some optimum heating conditions to give the greatest wet strength at less sacrifice of dry embrittlement.

Firstly, refiner groundwood pulp (RGP) was prepared from a birchwood and the component of hemicellulose or/and lignin was removed from it at different rate¹²⁾. Secondly, after handsheets prepared from beaten pulps of three-freeness stages, were heat-treated under various conditions, the tests were carried out on dry and wet strength, brightness, dimensional stability, pH, bulk and IR spectrum of the sheets.

I. Experimental

1. Material Used

The material used for this work was chips of a birchwood (*Betula platyphylla* SUKATCH. var. *japonica* HARA) which was obtained at Teshio Experimental Forests of Hokkaido University, in August, 1964. A chemical composition of the wood is shown in Table 1. Alpha cellulose content was determined from chlorite holocellulose prepared by WISE's method¹⁴²⁾. TAPPI standard methods were used for the other determination³⁶⁾.

Table 1. Chemical composition of birchwood (%)

Ash	Extractives with				Holo-cellulose	α -Cellulose	Total pentosan	Methyl pentosan	Lignin
	cold water	hot water	1% NaOH	alcohol-benzene					
0.14	1.5	3.4	18.3	2.5	79.2	50.1	25.1	1.6	18.4

2. Pulping

Four kg of air-dried birch chips were furnished for the preparation of pulp. After 24 hour-immersion into cold water, the chips were fiberized in a Sprout-Waldron laboratory refiner equipped with 12527A plates, the clearance of which was set at 0.8, 0.3 and 0.1 mm successively. Chip consistency was maintained at 8%. The pulp was screened through a 12-cut flat screen. The rejects were also fiberized in the same manner at 0.05 mm clearance. The yield of this RGP was determined by usual method.

3. Preparation and Analysis of Various Pulps

To obtain the pulps containing hemicellulose at different rate the RGP was separately treated with 1, 5, 10, and 20% sodium hydroxide solution at room temperature for 1 hour¹²⁾. On the other side, to obtain the pulps containing lignin at different rate it was treated with acetic acid-sodium chlorite at 75°C for 1 hour once, twice, thrice and four times, separately according to the WISE's method¹²⁾. Furthermore, the pulp treated thrice with the chlorite was similarly treated with 1, 5 and 10% sodium hydroxide solution¹²⁾. All the pulps were thoroughly washed with cold water and in case of alkali-treatment, moreover washed with dilute acetic acid and water. Thus, 12 kinds of pulps were

Table 2. Preparing condition, yield and composition of various pulps (%)

No.	Preparing condition	Yield	Holocellulose		α -Cellulose		Pentosan		Lignin	
			in pulp	based on RGP	in pulp	based on RGP	in pulp	based on RGP	in pulp	based on RGP
1	RGP	100	85.9	85.9	45.3	45.3	25.4	25.4	18.1	18.1
2	1% NaOH extraction	88.2	80.7	71.2	44.0	38.8	21.5	19.0	20.0	17.6
3	5% NaOH extraction	74.8	74.8	56.0	42.9	32.1	10.6	7.9	21.3	15.9
4	10% NaOH extraction	70.3	74.2	52.2	42.0	29.5	8.5	6.0	21.3	15.0
5	20% NaOH extraction	72.3	72.2	52.2	34.0	24.6	8.3	6.0	22.1	16.0
6	Delignified with NaClO ₂ , once	90.0	90.6	81.5	50.2	45.2	26.9	24.2	10.4	9.4
7	" , twice	85.4	94.4	80.6	52.4	44.7	27.9	23.8	6.8	5.8
8	" , thrice	82.7	95.8	79.2	52.9	43.7	28.7	23.7	3.7	3.1
9	" , four times	77.6	96.0	74.5	55.4	43.0	27.0	21.0	2.2	1.7
10	Delignified thrice + 1% NaOH extraction	62.3	98.1	61.1	61.7	38.4	17.1	10.7	2.5	1.6
11	" + 5% NaOH extraction	48.3	99.0	47.8	65.0	31.4	11.1	5.4	1.4	0.7
12	" +10% NaOH extraction	41.5	100.0	41.5	63.3	26.3	2.0	0.8	0.8	0.3

prepared, as summarized in Table 2.

The main components of those pulps were analyzed according to the standard method³⁶⁾.

4. Beating and Sheet Formation

The pulps were beaten in a Rabus-type beater, and obtained at three-freeness stages of non-beating, 400 and 200 mℓ with a Canadian Standard tester respectively.

Ten to 15 handsheets were prepared in a TAPPI sheet machine from each pulp at each freeness.

5. Heat Treatment

The conditions of heat treatment used for the handsheets were properly selected by combinations as follows⁴⁷⁾: temperature in a hot air circulation oven...105, 130, 155 and 180°C; time...1, 3 and 5 hours; pressure...atmospheric and reduced pressure (15 mmHg). In the latter the treatment was carried out in a desiccator with glass cock connected to aspirator.

6. Testing Procedures of Physical Properties

After the handsheets untreated and heat-treated were conditioned at 20°C and 65% RH, brightness by Hunter, tensile, bursting and tearing strength were measured according to TAPPI standard methods for dry handsheets³⁷⁾. The pH of some handsheets was measured with a glass electrode pH meter using the aqueous solution extracted from 0.5 g of the specimens with 50 mℓ of hot distilled water. The dimensional stability was calculated in terms of percentage thickness-increase in swelling by soaking into water at $23 \pm 2^\circ\text{C}$ for 10 min $\left(\frac{\text{thickness of the wet sheet} - \text{that of the dry sheet}}{\text{thickness of the dry sheet}} \times 100 \right)^{7)}$. The IR absorption spectra of some handsheets were recorded on a grating infrared spectrophotometer, using a KBr-pellet method. For wet strength, the specimens were similarly immersed for 10 min into water at $23 \pm 2^\circ\text{C}$. Wet tensile strength was determined as follows: each end of the specimen was glued to the kraft paper tab by adhesive and the one end was attached to the center of a frame and the other to a proper beaker with clamp. Load was applied to the specimen by admitting water to the beaker at constant rate of ca. 200 mℓ per min. The tensile load was measured by weighing it. Wet bursting and tearing strength were carried out with conventional testers using two and eight sheets of the specimens, respectively.

II. Results and Discussion

1. Yield and Chemical Components of Pulps

Yield of RGP was 84.6% on an average based on the dry chips. To minimize loss of components of the wood, a milder condition was adopted for defibration, but the yield was somewhat low unexpectedly¹²⁾.

Yield of the pulps is shown in Table 2, on the basis of the RGP. With increase of cold alkaline concentration for hemicellulose extraction, the yields (No. 2, 3 and 4) were gradually lowered, but the pulp treated with 20% alkali was higher by 2% in the yield than that of 10%. With increasing the number of chlorite treatment, the yield (No. 6, 7, 8 and 9) was also decreased. With alkaline extractions of delignified pulps the yields were extremely low.

Table 2 reveals also the content of main chemical components in the various pulps. The pulp of No. 1 shows the chemical composition of the RGP, the value of which is similar to that of the wood. It is understandable from the results of analysis that the alkaline extraction removed mainly hemicellulose and the chlorite treatment mainly lignin, respectively. However, these treatments removed more or less all the components, as shown from the values based on the RGP.

2. Physical Properties of Handsheets without Heat Treatment

Brightness and dry strength of pulp handsheets by non-heat treatment are shown in Table 3. Brightness of the RGP was 47.7% and it was a little lowered by alkaline extraction except in case of 20% alkali, while it was considerably elevated by the chlorite treatment. The handsheet of No. 12 showed the highest brightness. Generally, the brightness was slightly lowered with reduction of freeness.

Dry strength of the sheets from the unbeaten RGP and alkali-treated pulps were extremely low. Only No. 3 showed some weak strength. The strength of the sheets from chlorite treated pulps gradually increased with number of the treatment. However, the alkaline extraction of delignified pulp lowered again

Table 3. Brightness and dry strength of handsheets untreated

No.	Brightness (%)			Breaking length (km)			Burst factor			Tear factor		
	unbeaten	400	200	unbeaten	400	200	unbeaten	400	200	unbeaten	400	200
1	47.7	47.1	46.8	<0.3	<0.3	0.3	<0.1	<0.1	<0.1	<2	<2	<2
2	44.5	44.0	42.5	<0.3	1.7	2.2	<0.1	0.4	0.8	2	24	24
3	44.2	44.1	43.1	0.4	1.6	2.5	<0.1	0.4	0.9	10	26	24
4	42.2	41.1	40.4	<0.3	1.0	1.5	<0.1	0.3	0.2	<2	13	14
5	47.7	47.4	45.9	<0.3	0.9	1.3	<0.1	0.1	0.3	<2	12	8
6	49.4	49.2	49.0	<0.3	1.2	2.2	0.2	0.2	0.5	3	25	19
7	55.9	55.2	55.6	0.3	2.4	4.2	0.2	0.8	1.8	<2	31	37
8	58.5	56.8	55.8	2.2	5.4	6.5	0.5	2.9	4.2	40	47	40
9	66.5	61.0	57.3	3.5	5.4	6.2	1.3	2.1	4.9	52	48	46
10	58.9	57.0	54.7	4.5	5.4	6.4	2.5	4.3	5.3	70	63	60
11	66.9	65.7	64.0	3.4	5.4	5.8	0.8	3.8	4.1	52	63	58
12	74.2	74.2	67.8	1.1	2.8	3.3	0.2	1.6	2.3	15	55	50

the strength with the concentration. Dry breaking length and burst factor were high in lower freeness. Generally, the beaten pulps containing higher hemicellulose and lower lignin showed a good strength, while those of both low hemicellulose and low lignin content revealed a weak strength, even if this pulp has high content of alpha cellulose, which might be partially degraded by treatment with the solution of higher alkaline concentration.

3. Effect of Heat Treatment on Physical Properties of Handsheets

a. Hydrogen ion concentration, bulk, dimensional stability, brightness and IR spectra.....Hydrogen ion concentration of the water extract of handsheets treated at 105°C, and 180°C under reduced pressure, is shown in Table 4, together with the pH of the extract of untreated sheets. An insignificant pH change among the sheets containing different components was recognized, but the pH was somewhat lowered with raising of the temperature and duration of heating time. The low pH seems to be caused by small quantities of organic acid produced from the pulp components owing to its degradation by heat.

Heat treatment hardly effected bulk of the sheets as shown in Table 5; a little loss of weight could be present, but as shrinkage might be also considered to some extent, thus it seems that the bulk did not almost vary by counterbalancing these two factors. However, the bulk is considerably changed by the chemical composition of pulps; namely the sheets of high lignin content had always high bulk and those of high holocellulose content had low one, because of close fiber to fiber bonding in the sheets.

Percentage thickness-swelling by soaking in water is shown in Table 6, as

Table 4. pH of extract from handsheets at 200 ml CSf

No.	Untreated	105°C A. P.		180°C R. P.		
		3 hr	5 hr	1 hr	3 hr	5 hr
1	5.6	5.4	5.3	5.2	4.7	4.5
2	6.0	4.9	4.8	5.8	5.4	5.4
3	6.0	5.6	4.9	5.9	5.5	4.8
4	6.0	5.4	5.3	5.3	5.6	4.6
5	5.6	5.6	5.6	5.3	4.8	4.6
6	5.6	5.3	5.5	5.0	4.8	4.7
7	5.5	4.9	4.8	5.0	4.9	4.4
8	5.0	4.6	4.8	4.6	4.8	4.4
9	5.5	4.9	4.7	4.7	4.5	4.3
10	5.5	4.8	5.0	4.6	4.5	4.2
11	5.6	5.2	5.1	4.7	4.4	4.2
12	5.8	5.5	5.4	4.8	4.6	4.4

A. P.; Under atmospheric pressure.

R. P.; Under reduced pressure.

a criterion of dimensional stability. The swelling of No. 1 was minimum, while that of No. 8 was maximum; fibers of the former were covered with lignin which is more hydrophobic than the other components, and the latter had the highest hemicellulose which is hygroscopic. In general, the sheets of high lignin content showed a low swelling and vice versa. However, as heat treat-

Table 5. Bulk of handsheets at 200 ml CSf

No.	Untreated	105°C A.P.		180°C R.P.		
		3 hr	5 hr	1 hr	3 hr	5 hr
1	3.1	3.5	4.1	3.8	4.0	3.8
2	3.1	2.9	2.9	2.6	3.2	2.8
3	2.0	2.3	2.4	2.3	2.3	2.3
4	2.3	2.4	2.6	2.3	2.4	2.3
5	2.3	2.4	2.5	2.4	2.3	2.2
6	3.2	3.3	3.0	2.7	2.7	2.7
7	2.9	2.6	2.6	2.3	2.2	2.0
8	1.8	2.0	2.0	1.6	1.7	1.7
9	1.9	1.9	1.7	1.4	1.3	1.5
10	1.9	1.5	1.5	1.4	1.5	1.5
11	1.4	1.5	1.5	1.3	1.4	1.4
12	1.6	1.7	1.6	1.4	1.3	1.6

A. P.; Under atmospheric pressure.

R. P.; Under reduced pressure.

Table 6. Thickness swelling of handsheet at 200 ml CSf (%)

No.	Untreated	105°C A.P.		180°C R.P.		
		3 hr	5 hr	1 hr	3 hr	5 hr
1	21	20	18	14	12	9
2	28	26	18	19	20	20
3	54	47	25	19	15	14
4	46	43	23	19	18	15
5	41	41	24	25	17	20
6	36	30	29	21	20	19
7	45	42	34	35	23	23
8	79	63	50	30	24	23
9	78	65	60	30	25	23
10	40	40	35	29	20	21
11	55	44	33	28	20	21
12	55	45	32	28	14	11

A. P.; Under atmospheric pressure.

R. P.; Under reduced pressure.

ment converts partially hemicellulose to water-repellent hydrophobic material owing to hornization of it²⁷⁾, the swelling of the treated sheet much decreased. The sheet of high alpha cellulose content (No. 12) also showed a considerably low swelling by the treatment. It is noticed from the results dimensional stabilization of the sheets was much improved by heat treatment.

Brightness of the sheets prepared at 200 ml CSf is shown in Table 7. Comparatively low brightness of the sheets was not changed by heat treatment, but high brightness of holocellulose-rich sheet which corresponds to paper of

Table 7. Brightness of handsheets at 200 ml CSf (%)

No.	Untreated	105°C R.P.			180°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	46.8	47.5	47.8	44.8	37.8	33.0	28.2
2	42.5	42.8	42.8	41.0	34.8	26.0	22.1
3	43.1	44.2	44.0	44.4	32.0	29.1	25.3
4	40.4	41.8	42.4	40.1	38.0	32.2	27.8
5	45.9	46.6	47.0	46.2	38.5	33.2	28.0
6	49.0	49.2	48.5	49.8	27.3	20.8	18.3
7	55.6	54.1	54.2	54.2	26.0	19.1	16.3
8	55.8	55.7	55.5	55.3	20.5	14.4	12.1
9	57.3	55.6	55.6	55.2	19.7	12.5	10.1
10	54.7	48.8	48.3	47.9	22.6	13.6	11.1
11	64.0	61.0	58.7	59.2	31.8	21.2	17.4
12	67.8	67.6	66.6	66.3	42.8	30.8	26.5

R. P. ; Under reduced pressure.

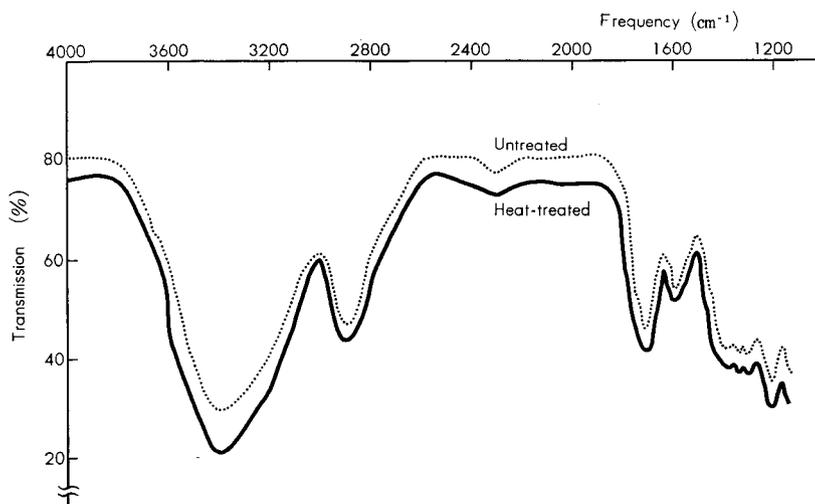


Fig. 1. Infrared spectra of No. 1 sheets untreated and treated at 180°C for 5 hr.

fine quality in the composition, was considerably decreased by the treatment. Drying at 105°C did not almost influence the change of brightness. Fall of the brightness was mainly caused by caramelization of polysaccharides especially hemicelluloses in the sheets by heat. Brightness of No. 12 which slightly contained both lignin and hemicellulose was not so much lowered by the treatment.

Infrared absorption spectra of some sheets obtained by heat-treatment are shown in Fig. 1, 2, and 3. The spectrum was recorded in the region of 4000 to

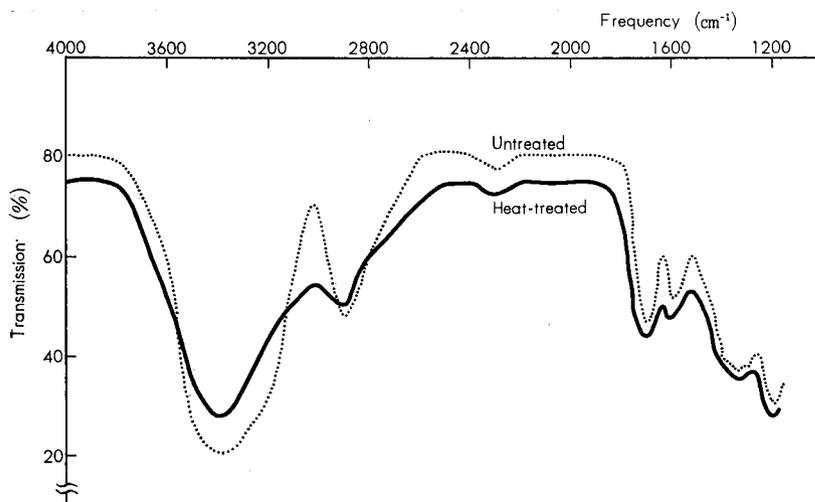


Fig. 2. Infrared spectra of No. 8 sheets untreated and treated at 180°C for 5 hr.

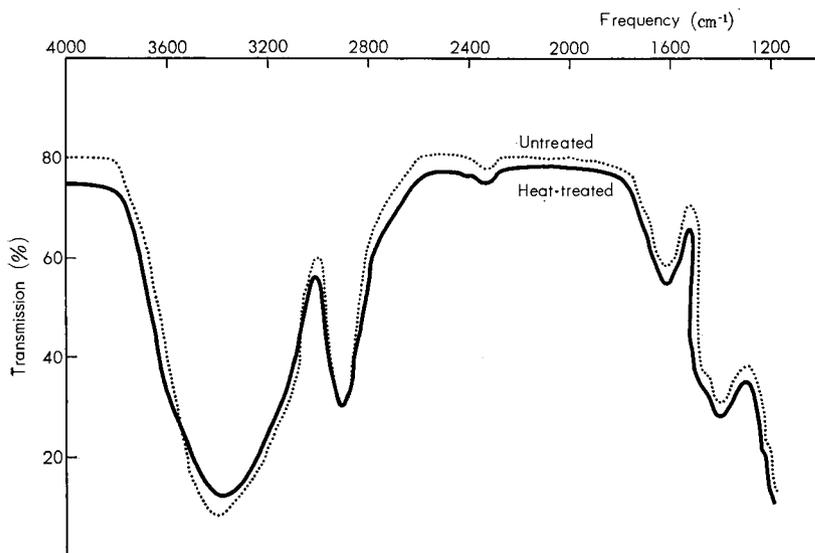


Fig. 3. Infrared spectra of No. 12 sheets untreated and treated at 180°C for 5 hr.

1200 cm^{-1} to investigate mainly behavior of hydroxyl group. Fig. 1 shows the spectra of two RGP sheets untreated and treated at 180°C for 5 hours under reduced pressure. There is recognized little difference between them, while between the treated and untreated sheets of No. 8 a little different absorbance is observed in band near 3300 cm^{-1} of O-H stretching vibration, though they have the almost same intensity in band of 2900 cm^{-1} of C-H stretching vibra-

Table 8. Dry breaking length of handsheets unbeaten (km)

No.	Untreated	130°C R.P.			155°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
2	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
3	0.4	0.3	<0.3	<0.3	0.5	<0.3	<0.3
4	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
5	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
6	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
7	0.3	0.5	0.5	0.6	0.7	0.3	0.3
8	2.2	2.4	2.9	2.3	2.2	2.4	2.1
9	3.5	3.8	3.6	4.2	3.4	3.7	3.5
10	4.5	6.0	5.6	5.9	4.8	5.2	4.3
11	3.4	3.4	3.5	3.0	2.4	2.8	2.1
12	1.1	0.6	0.6	0.6	0.6	0.7	0.5

R.P.: Under reduced pressure.

Table 9. Dry breaking length of handsheets at 400 ml CSf (km)

No.	Untreated	155°C A.P.			155°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
2	1.7	1.6	1.7	1.7	1.8	2.1	1.9
3	1.6	1.6	1.7	1.7	2.0	1.9	1.8
4	1.0	0.9	1.2	1.1	1.4	1.4	1.1
5	0.9	0.8	0.7	1.0	0.9	1.1	1.0
6	1.2	1.1	1.2	1.2	1.3	1.4	1.0
7	2.4	2.2	2.5	3.3	2.9	2.7	2.6
8	5.4	4.9	4.7	4.4	5.9	5.4	4.9
9	5.4	4.7	4.5	4.1	5.4	5.1	4.9
10	5.4	6.7	6.5	5.9	7.0	7.0	6.2
11	5.4	4.9	5.6	4.5	6.1	5.9	4.9
12	2.8	2.7	2.9	2.1	2.9	3.0	2.5

A.P.; Under atmospheric pressure.

R.P.; Under reduced pressure.

tion (Fig. 2). Fig. 3 shows a similar result to that of Fig. 2. This means these sheets were somewhat changed in holocellulose component by heat and decreased in hydroxyl group.

b. Dry strength.....Dry breaking length of the sheets heat-treated under various conditions is shown in Tables 8, 9 and 10 according to their freeness of unbeating, 400 and 200 ml, respectively. Unbeaten pulp sheets of high lignin content hardly showed the strength. Table 8 shows higher strength was

Table 10. Dry breaking length of handsheets at 200 ml CSf (km)

No.	Untreated	105°C R.P.			180°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	0.3	<0.3	0.5	0.5	0.4	0.5	0.4
2	2.2	1.8	2.2	2.6	2.5	3.1	2.9
3	2.5	1.9	2.0	2.6	3.6	2.8	3.1
4	1.5	1.8	1.4	2.1	2.2	2.0	1.8
5	1.3	1.1	1.0	1.3	1.6	1.6	1.1
6	2.2	1.8	1.9	2.2	2.3	2.4	1.6
7	4.2	3.9	3.9	3.9	4.3	3.7	3.8
8	6.5	6.2	6.4	6.7	6.4	5.6	5.0
9	6.2	5.8	6.4	6.7	6.9	4.7	4.6
10	6.4	6.9	6.6	6.4	7.9	5.8	5.9
11	5.8	5.7	5.7	5.9	7.2	5.6	5.1
12	3.3	3.6	3.2	3.4	4.1	3.1	2.9

R. P.; Under reduced pressure.

Table 11. Dry burst factor of handsheets unbeaten

No.	Untreated	130°C R.P.			155°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
3	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5	<0.1	—	—	—	<0.1	<0.1	—
6	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
7	0.2	0.2	0.1	<0.1	0.1	<0.1	<0.1
8	0.5	0.8	0.8	0.6	0.6	0.6	0.6
9	1.3	0.6	1.5	1.5	1.4	1.5	1.4
10	2.5	3.0	2.9	3.0	2.3	2.3	2.4
11	0.8	1.1	1.1	0.9	0.7	0.8	0.8
12	0.2	0.2	0.2	<0.1	<0.1	<0.1	0.1

R. P.; Under reduced pressure.

generally obtained even by the treatment at 130°C for 1 hour under reduced pressure. The duration of the heating time gradually decreased the strength, especially at higher temperature. At 400 ml freeness (Table 9), the same tendency of the strength was observed as the case of unbeating sheets. Furthermore, Table 9 also shows difference of the strength between atmospheric and reduced pressure. It is explained that fall of the strength involved in oxidation

Table 12. Dry burst factor of handsheet at 400 ml CSf

No.	Untreated	155°C A.P.			155°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2	0.4	0.3	0.2	0.3	0.3	0.4	0.3
3	0.4	0.4	0.4	0.3	0.2	0.4	0.3
4	0.3	0.3	0.2	0.2	0.1	<0.1	0.3
5	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
6	0.2	0.1	0.1	0.2	0.3	<0.1	0.2
7	0.8	0.8	0.8	0.7	1.3	0.6	0.6
8	2.9	2.7	2.4	2.6	2.7	2.2	2.4
9	2.1	2.0	1.9	2.0	2.3	2.0	1.7
10	4.3	4.3	4.1	4.0	4.3	3.9	3.8
11	3.8	3.8	3.2	3.3	3.8	3.5	3.3
12	1.6	1.5	1.4	1.5	1.5	1.5	0.5

A.P.; Under atmospheric pressure.

R.P.; Under reduced pressure.

Table 13. Dry burst factor of handsheets at 200 ml CSf

No.	Untreated	105°C R.P.			180°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	<0.1	<0.1	0.1	<0.1	<0.1	0.1	0.1
2	0.8	0.6	0.6	0.7	0.6	0.5	0.7
3	0.9	0.6	0.6	0.7	0.9	0.8	0.8
4	0.2	0.4	0.3	0.5	0.5	0.6	0.6
5	0.3	0.2	0.2	0.3	0.4	0.3	0.4
6	0.5	0.4	0.4	0.6	0.5	0.7	0.5
7	1.8	1.5	1.4	1.3	1.4	1.5	1.3
8	4.2	4.0	3.2	2.7	2.7	2.4	1.6
9	4.9	4.4	3.8	3.3	2.5	2.4	1.8
10	5.3	5.4	5.2	5.0	3.8	2.8	2.5
11	4.1	4.4	4.1	4.0	4.0	3.7	2.4
12	2.3	2.1	1.9	2.1	2.2	1.7	1.4

R.P.; Under reduced pressure.

of holocellulose caused by the heat treatment was to some extent prevented by elimination of air namely by reduced pressure. Table 10 shows that the drying at 105°C scarcely changed the breaking length even though heating time was extended, but the higher temperature (180°C) decreased it with increasing the time. The highest value of all, however, was given by the treatment at 180°C for 1 hour.

Table 14. Dry tear factor of handsheets unbeaten

No.	Untreated	130°C R.P.			155°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	<2	3	2	3	<2	<2	<2
2	2	7	8	8	6	5	5
3	10	10	8	9	11	11	6
4	<2	3	3	<2	<2	<2	<2
5	<2	<2	<2	<2	<2	<2	<2
6	3	3	2	<2	<2	5	<2
7	<2	17	15	7	18	5	3
8	40	37	41	35	36	37	38
9	52	45	44	45	41	42	40
10	70	61	55	53	58	49	50
11	52	46	47	44	38	38	39
12	15	21	23	16	14	15	13

R. P.; Under reduced pressure.

Table 15. Dry tear factor of handsheets at 400 ml CSF

No.	Untreated	155°C A.P.			155°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	<2	<2	3	6	<2	6	3
2	24	20	22	21	24	23	16
3	26	14	28	21	21	25	17
4	13	20	16	19	18	16	14
5	12	15	11	17	17	15	10
6	25	17	14	18	20	17	19
7	31	26	25	26	32	23	26
8	47	38	19	28	35	20	24
9	48	52	38	29	57	33	28
10	63	48	51	45	56	55	46
11	63	43	42	42	45	50	43
12	55	38	42	31	36	38	28

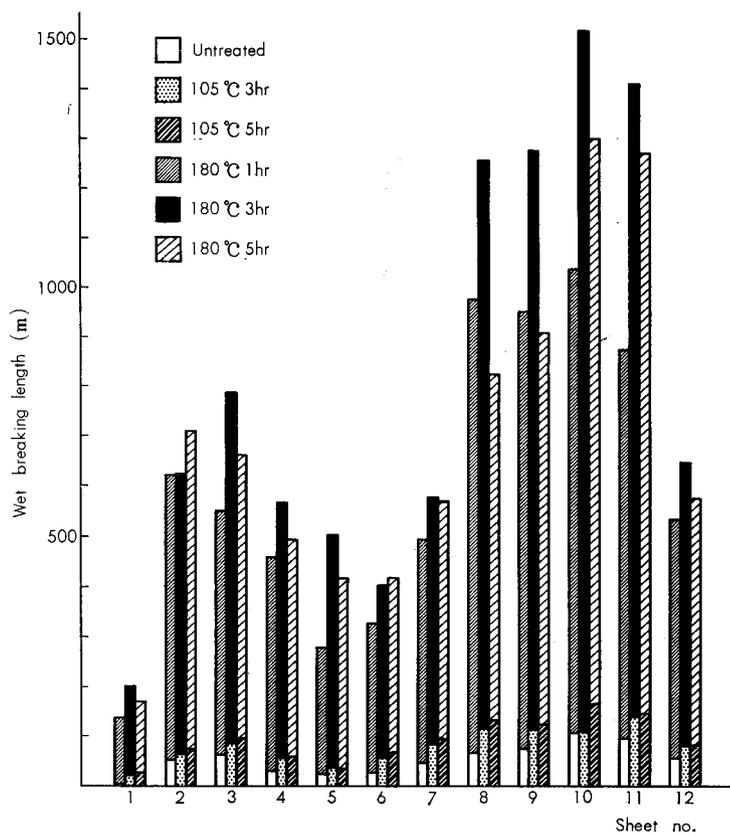
A. P.; Under atmospheric pressure.

R. P.; Under reduced pressure.

Table 16. Dry tear factor of handsheets at 200 ml CSf

No.	Untreated	105°C R.P.			180°C R.P.		
		1 hr	3 hr	5 hr	1 hr	3 hr	5 hr
1	<2	9	3	6	6	<2	<2
2	24	31	27	23	18	18	17
3	24	35	29	29	33	26	16
4	14	34	22	21	19	16	18
5	8	17	15	15	18	15	16
6	19	31	21	21	17	18	14
7	37	44	32	29	22	24	17
8	40	48	42	33	34	39	17
9	46	62	41	52	38	19	18
10	60	69	66	63	54	30	19
11	58	64	70	57	44	31	35
12	50	55	42	40	40	32	28

R.P.; Under reduced pressure.

**Fig. 4.** Wet breaking length of handsheets heat-treated.

Dry burst factor of the heat-treated sheets is shown in Tables 11, 12 and 13. In general, this strength was decreased with raising of the temperature and duration of heating time, because of producing the embrittlement of the sheets by heat.

Dry tear factor of the sheets is shown in Tables 14, 15 and 16. The similar decrease in the strength with raising of the temperature was observed.

c. Wet strength..... Though all the specimens were immersed in water only for 10 min, this seemed to be sufficient time for wetting the sheets

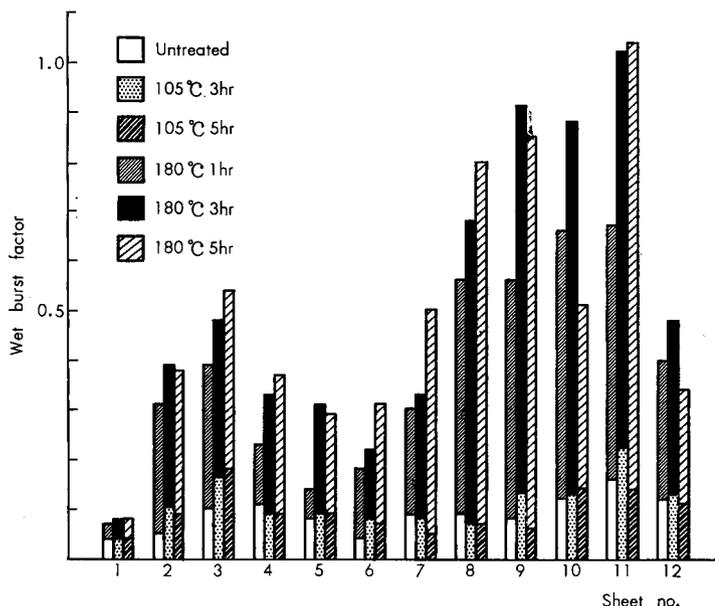


Fig. 5. Wet burst of handsheets heat-treated.

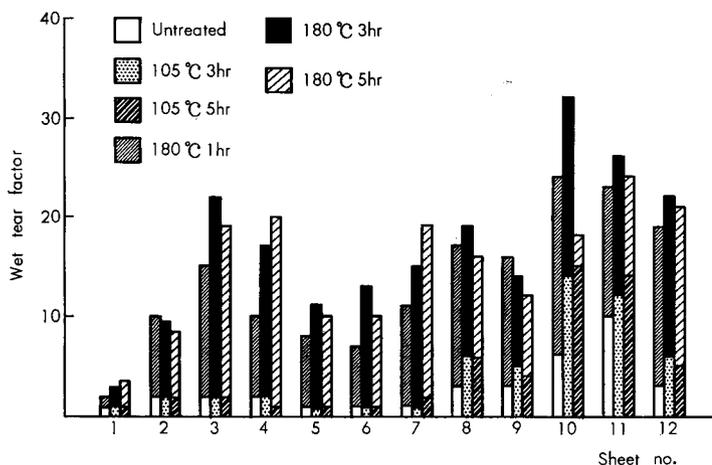


Fig. 6. Wet tear factor of handsheets heat-treated.

tested. TAPPI standards⁴⁾ describe the procedure for determining the wet tensile strength of paper after complete saturation with water until the specimen is wetted throughout and a stable minimum strength value is obtained. Therefore, this time might be unsatisfactory at that point. However, by the short immersion period it was possible to compare the heat-treated sheet with the untreated one of extremely low wet strength. Wet breaking length of the sheets is shown in Fig. 4. Compared with the dry strength, it was very low. Heat treatment, however, increased remarkably the strength and the sheets of high dry strength showed high wet strength. The best treating time at 180°C was found to be 3 hours. The 5-hour treated sheets somewhat decreased the strength. Untreated sheets retained only 1 to 3% of their dry strength by wetting, (for examples, $\frac{\text{wet breaking length}}{\text{dry breaking length}}$ in No. 3: $\frac{59}{1600} \times 100 = 3.1\%$, that in No. 8: $\frac{68}{5400} \times 100 = 1.2\%$), but heat-treated sheets obtained wet strength of 20 to 30% of the dry strength, ($\frac{\text{wet breaking length}}{\text{dry breaking length}}$ in No. 3 treated at 180°C for 3 hours: $\frac{785}{2800} \times 100 = 28\%$, that in No. 8 of the same treatment: $\frac{1253}{5600} \times 100 = 22\%$). If paper possessing a wet tensile strength of more than 15% of the dry strength is considered a wet strength paper⁴⁾, the heat treatment seems to be a simple and effective method.

Wet burst and tear factor of the sheets are shown in Fig. 5 and 6, respectively. The similar tendency was observed to wet breaking length. The severe treatment of 5 hours at 180°C also a little lowered these wet strength.

Mechanism of wet strength-increase by heat treatment is considered as follows: Owing to a partial hornization of polysaccharides, especially hemicellulose in the pulp sheet composition, caused by heat treatment, the sheet becomes to some extent hydrophobic or water-repellent, and furthermore new formation of interfiber and hydrogen bonding by the treatment appears to be involved^{4b)}. It would be conclusively stated these synergistic effect could improve the wet strength and dimensional stability.

Conclusions

Twelve kinds of pulps containing different components were prepared from birch refiner-groundwood pulp and these handsheets obtained were heat-treated at 105 to 180°C for 1 to 5 hours under atmospheric or reduced pressure. The physical properties were tested and following conclusions were obtained.

1. Hydrogen ion concentration of the water extract of handsheets was somewhat lowered with raising of the temperature and duration of the time, caused by small quantities of organic acid produced from the pulp components. Bulk of the sheets did not almost vary with heat treatment. Dimensional sta-

bility in swelling was extremely increased by the treatment, probably by partial converting hemicellulose to water-repellent material and decreasing hydrophilic hydroxyl group. Infrared absorption spectra proved that some pulps strongly heat-treated were a little low in hydroxyl group content.

2. Breaking length of the dry sheets was a little increased by heat treatment. However, duration of the time at higher temperature slightly lowered the strength. The highest dry breaking length was obtained by the treatment at 180°C for 1 hour. In general, dry burst and tear factor decreased with raising of the temperature and duration of the time, because of producing the embrittlement of the sheet. The heat-treatment under reduced pressure did not so remarkably improve the strengths, compared with those treated under atmospheric pressure.

3. Wet breaking length was very low, compared with dry one. But heat treatment remarkably increased the strength, and the sheet of high dry strength naturally showed the high wet one. The highest wet breaking length was obtained by the treatment at 180°C for 3 hours. The 5-hour treatment decreased the strength to some extent. The heat treatment employed here showed wet breaking length corresponding to about 20 to 30% of the dry strength. Wet burst and tear factors were similarly increased by the treatment.

4. Heat treatment proved to be considerably effective on wet strength and dimensional stabilization by the less sacrifice of brightness and some dry strength.

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摘 要

パルプ紙葉の物理的性質におよぼす熱処理の効果をしらべるために、シラカンバ (*Betula platyphylla* SUKATCH. var. *japonica* HARA) の RGP から、種々の組成をもつ 12 種類のパルプ紙葉を調製し、温度 105°C から 180°C、時間 1 時間から 5 時間の範囲で、常圧および減圧の条件で熱処理をおこない、処理紙葉の乾燥および湿潤強度、白色度、pH、かさ、水に対する厚さ膨潤率および IR 吸収スペクトルを測定した。

その結果はつぎのとおりである。

1. 紙葉の熱水抽出液の pH は、処理温度の上昇および時間の経過とともに低下した。かさは熱処理によってほとんど変化しなかった。一方膨潤率は著しく低下し、紙の寸法安定性が向上したことを示している。これは恐らく、パルプ中の親水性ヘミセルロースの部

分的な角質化による疎水性物質への変化と考えられ、水酸基の減少は IR 吸収スペクトルから推定された。

2. 乾燥裂断長は熱処理によりわずかに増加したが、高温で長時間処理した場合は再び低下した。最高の裂断長は 180°C, 1 時間処理でえられた。乾燥比破裂度と比引裂度は、温度上昇および時間の経過とともに、紙葉のもろさを増すため低下した。

3. 未処理紙葉の湿潤強度は著しく低い、熱処理により改善され、とくに乾燥強度の高いものは顕著であった。最高の裂断長は 180°C, 3 時間の処理でえられ、5 時間処理ではわずかに低下した。この処理範囲内では、いずれのパルプも乾燥裂断長の 20 ないし 30 %の湿潤裂断長をうることができた。湿潤比破裂度と比引裂度も同様に熱処理により改善された。

4. 以上のことから、熱処理は湿潤強度と寸法安定性に対して、かなり効果があることが示されたが、白色度と乾燥強度を一般には低下させた。